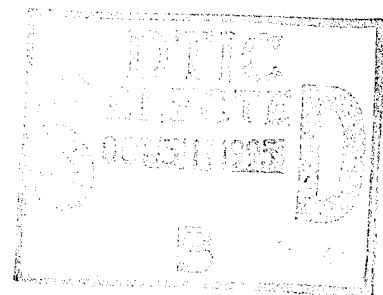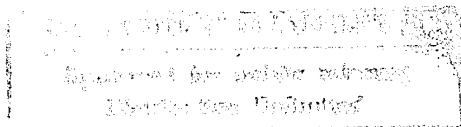OFFICE OF NAVAL RESEARCH

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Light Induced Cluster-to-Organic-Acceptor Charge Transfer
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13. ABSTRACT (Maximum 200 words)

The molecular cluster, $[Cd_4(S-C_6H_4NO_2)_{10}]\{N(CH_3)_4\}_2$, exhibits an intense near-UV absorption that is absent in the corresponding benzenethiolate cluster. Resonance Raman and electronic Stark effect studies show that the absorption feature originates from a pair of closely spaced cluster-to-nitrobenzene charge-transfer transitions. The lower lying charge-transfer excited state is weakly luminescent. Time resolved luminescence measurements yield a nonradiative decay or back electron transfer rate (nitrobenzene to cluster) of 3.3×10^8 s^{-1}. Further analysis of resonance Raman scattering reveals that at least 7 vibrational modes are coupled, in a Franck-Condon sense, to the electron transfer process. In terms of absolute normal coordinate displacement, the two most important modes are Cd-S and N-O stretches.

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Light induced charge transfer from nanocrystalline semiconductor particle dispersions or films to molecular acceptors forms an integral part of potential or emerging energy conversion strategies[1] and water decontamination strategies.[2] Generally these strategies involve semiconductor bandgap excitation, followed by charge separation via surface localization and ultimately, interfacial hole (valence band) or electron (conduction band) transfer.[1-3] Here we describe in preliminary terms an alternative *direct* study of charge transfer between a cadmium-sulfide based cluster and a covalently attached molecular acceptor (nitrobenzene).[4] The system examined, $Cd_4(S\text{-}NB)_{10}{}^{2-}$ (1) (S-NB is the 4-nitrothiophenol anion), is a simple derivative of $Cd_4(SC_6H_5)_{10}{}^{2-}$ (2). Synthesis of the latter has been described by Dance and co-workers.[5a,6] Cluster 2 (and by inference, 1) is among the smallest of several well-defined cadmium/sulfur (thiolate) clusters[5,7] and is the smallest to feature the adamantanoid structure of bulk cadmium sulfide. Much of the current interest in small clusters centers on optical manifestations of "quantum confinement" phenomena,[8,9] where the magnitudes of the phenomena are necessarily cluster size dependent. Quantum confinement should also play a role in charge transfer (CT) processes. In any case, covalent attachment of the acceptor to the cadmium-sulfide cluster leads to intense donor-acceptor CT absorption. The high absorption intensity, in turn, provides a basis for weak, but detectable, CT emission, and for the exploitation of other informative spectral methods.

Figure 1 compares electronic absorption spectra for 1 and 2 in MeOH as solvent. The pertinent features are (a) a far UV absorption (common to both) that we assign to overlapping sulfur-to-cadmium charge transfer and

(nitro)thiophenolate π-π^* transitions, and (b) a near UV absorption (λ_{max} = 376 nm), observed only for **1** and assigned as a cluster-to-nitrobenzene charge-transfer transition (shown schematically in eq. 1). The extremely large extinction for the feature at 395 nm (ε = 136,000 $M^{-1}cm^{-1}$) no doubt reflects both the multiplicity of nearly degenerate electron acceptors and the strong pi interaction through the benzene thiolate.

$$\text{(1)}$$
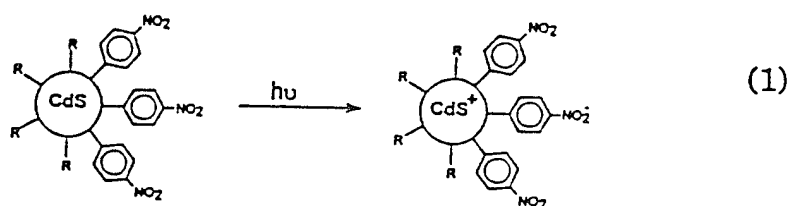
The longer wavelength charge transfer assignment has been confirmed via electric field effect (electronic Stark effect) measurements[10,11] on isotropic samples in a 1:5 (v:v) CH_3CN:methyltetrahydrofuran glass (ca. 77 K). While the Stark spectrum in Figure 2 exhibits the expected squared dependence of intensity upon field strength, it appears – at first glance – to be dominated by a first derivative, rather than second derivative component of the absorbance spectrum. (A substantial second derivative component is expected when significant charge-transfer effects, and therefore, ground-state/excited-state dipole moment differences, exist.) A more thorough evaluation shows that the spectrum is actually comprised chiefly of interfering second-derivative components from two overlapping electronic transitions. Two charge transfer transitions are, in fact, expected based on distinct "bridging" (Cd-SR-Cd) and "capping" (Cd-SR) thiolate geometries.[5a] Quantitative analysis of the Stark experiment is in progress.

Additional experiments involving normal and resonance Raman scattering

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(514.5 and 351 nm excitation, respectively) provide specific information about vibrations coupled to the charge transfer reaction. From the excitation wavelength dependence of the intensity of the scattering spectrum, several modes are clearly resonance (charge-transfer transition) enhanced. Analysis of scattering intensities (351 nm excitation; instrument response corrected) using time-dependent wavepacket propagation methods,[12,13] yields the estimates for normal coordinate displacements (Δ) shown in Table I.[14] These displacements are identically those required in a Franck-Condon sense for cluster-to-nitrobenzene charge transfer.[15] Notably, the largest displacements are associated with Cd-S and N-O stretches. Also shown in Table I are estimated contributions by each mode to the total vibrational reorganization energy (χ_{vib}) for reaction 1.

Figure 3 shows that **1** emits from the cluster-to-acceptor CT excited state, with an apparent Stoke shift of 7,000 cm^{-1}. Time resolved measurements (single photon counting, based on excitation at 380 nm with the frequency-doubled output of a mode-locked Ti:sapphire laser) yielded an excited state decay time of 3.0 ns. We have yet to perform fluorescence quantum yield measurements. The yield, however, clearly is small. It follows that the decay kinetics must be dominated by a nonradiative process – presumably back electron transfer. On that basis, k_{ET}(eq 1) is 3.3 x 10^8 s^{-1}.

Electrochemical studies of **1** (cyclic voltammetry) reveal an irreversible oxidation at ca. 390 mV and an irreversible reduction at ca. –880 mV. These are assigned, respectively, as coordinated thiolate oxidation and nitrobenzene reduction. Corresponding measurements for **2** yield only the oxidation wave. For both **1** and **2** the expected Cd(II) reduction is evidently obscured by solvent

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reduction.

Finally, an alternative view of reaction 1 would be an intraligand charge-transfer transition that is simply perturbed by the replacement of the thiol proton by a cadmium ion. Indeed, the free thiol (protonated) also exhibits a broad and relatively intense near-UV absorbance (λ_{max} = 412 nm). On the other hand, for small species such as **1** – where the same atoms play the roles of core (cluster) and surface (capping) chalcogenide – the distinction between the two descriptions may not be particularly instructive. Clearly, however, for larger clusters of the type $Cd_xS_y(S-R)_z{}^{n-}$ a differentiation between core (quantum confined donor) and surface (isolated ligand like) charge transfer behavior is significant. For R = benzene, several well defined clusters of larger size are known.[5,7] For R = 4-nitrobenzene, however, we have thus far been unable to obtain the next two members of the adamantoid cluster series, i.e. $Cd_{10}S_4(S-NB)_{16}{}^{4-}$ and $Cd_{20}S_{13}(S-NB)_{22}{}^{8-}$ (although a somewhat larger cluster, as yet incompletely characterized, has been obtained[16]). The synthetic difficulties are probably related to the diminished Lewis basicity of 4-nitrothiophenolate in comparison to thiophenolate. Decreased basicity could lead to incomplete capping (say, for the Cd_{10} entity), thereby providing a thermodynamic incentive for aggregation and creation of clusters larger than those expected from the stoichiometries of the starting materials.[7b] In any case, we expect to be able to access intermediate and large clusters in a more systematic fashion by replacing 4-nitrothiophenolate with either 3-nitrothiophenolate or any of several possible nitrothionapthalates.

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3. However, see also: (a) Vrachnou, E.; Gratzel, M.; McEvoy, A.J. *J. Electroanal. Chem.* **1989**, *258*, 193. (b) Blackbourn, R.L.; Johnson, C.S.; Hupp, J.T. *J. Am. Chem. Soc.* **1991**, *113*, 1060. (c) Lu, H.; Prieskorn, J.N.; Hupp, J.T. *J. Am. Chem. Soc.* **1993**, *115*, 4927. (d) Tuerk, T.; Retsch, U.; Fox, M.A.; Vogler, A. *J. Phys. Chem.* **1992**, *96*, 3818. (e) Turek, T.; Retsch, U.; Fox, M.A.; Vogler, A. *Inorg. Chem.* **1992**, *31*, 1854.

4. We note the existence of prior studies involving metal-chalcogenide cluster to methyl viologen charge transfer (weak outer-sphere CT between ion-paired species)[3d,e] and metallocyanide to titanium dioxide charge transfer (colloidal particles exhibiting bulk electronic properties).[3a-c]

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6. **1** was synthesized as the tetramethylammonium salt by using Dance's method for **2**,[5a] except that (a) 4-nitrothiophenol (recrystallized from

CH$_2$Cl$_2$/hexanes) was used in place of thiophenol, and (b) the reaction mixture (MeOH solution) was heated to boiling to enhance solubility. The crude product was purified by recrystallization from CH$_3$CN. Yield: 63 %.
^{1}H NMR (300 MHz, CD$_3$CN) δ 7.64 (d, J = 9.0 Hz, 20H), 7.44 (d, J = 9.0 Hz, 20H), 3.05 (s, 24H). FAB(-)MS (m-NBA, m/e): 2065 {(M - [(CH$_3$)$_4$N])$^-$} (8), 1835 (15), 1415 (100). Anal. calcd. for C$_{68}$H$_{64}$N$_{12}$O$_{20}$S$_{10}$Cd$_4$: C, 38.20; H,3.09; N, 7.89. Found: C, 38.17; H, 3.01; N, 7.86.

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8. A quantum confinement description implies the existence of electronic band structure. The smallest thiolate-capped cluster clearly displaying such structure is apparently Cd$_{20}$S$_{13}$(SC$_6$H$_5$)$_{22}$$^{8-}$ (Herron, N.; Suna, A.; Wang, Y. *J. Chem. Soc., Dalton Trans.* **1992**, 2329). Species **1**, therefore, is probably best viewed as a limiting molecular analog of the larger quantum-confined entities.

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14. The analysis protocol was similar to that described in refs. 14 d and f. Briefly, optimized normal coordinate displacements were obtained from a simultaneous best fit of calculated scattering and luminescence spectra to

experimental spectra (where a full time-dependent analysis of initial state and final state wavepacket overlaps was employed). To reproduce the structureless emission spectrum (Figure 3) an empirical damping factor of 500 cm^{-1} and an E_{00} value of $22,050 \text{ cm}^{-1}$ were required. In any case, a fit based on emission (presumably a single electronic transition) rather than absorbance (multiple electronic transitions) was expected to circumvent, to some extent, complications (e.g., excess spectral broadening) associated with the existence of multiple, overlapping charge-transfer transitions. Neglected in the preliminary analysis were finite temperature effects and solvent reorganization effects. Eventual inclusion of the former will likely lead to a slight downward revision in the displacement estimate for the lowest frequency mode. Inclusion of the latter should lead to slight decreases in estimated displacements for all vibrational modes.

15. The three highest frequency modes are omitted from the scattering analysis because of their assignments as overtone and combination modes. Support for these assignments comes, in part, from the observation that enhancement of high frequency scattering is undetectable with 457.1 nm excitation. (It is detectable for lower frequency modes.) In comparison to

fundamental vibrations, combinations and overtones are expected to exhibit much narrower excitation profiles (and therefore, much weaker at scattering at 457.1 nm than at 351 nm). (See, for example: Nafie, L. A.; Stein, P.; Peticolas, W. L. *Chem. Phys. Lett.* 1971, *12*, 131.)
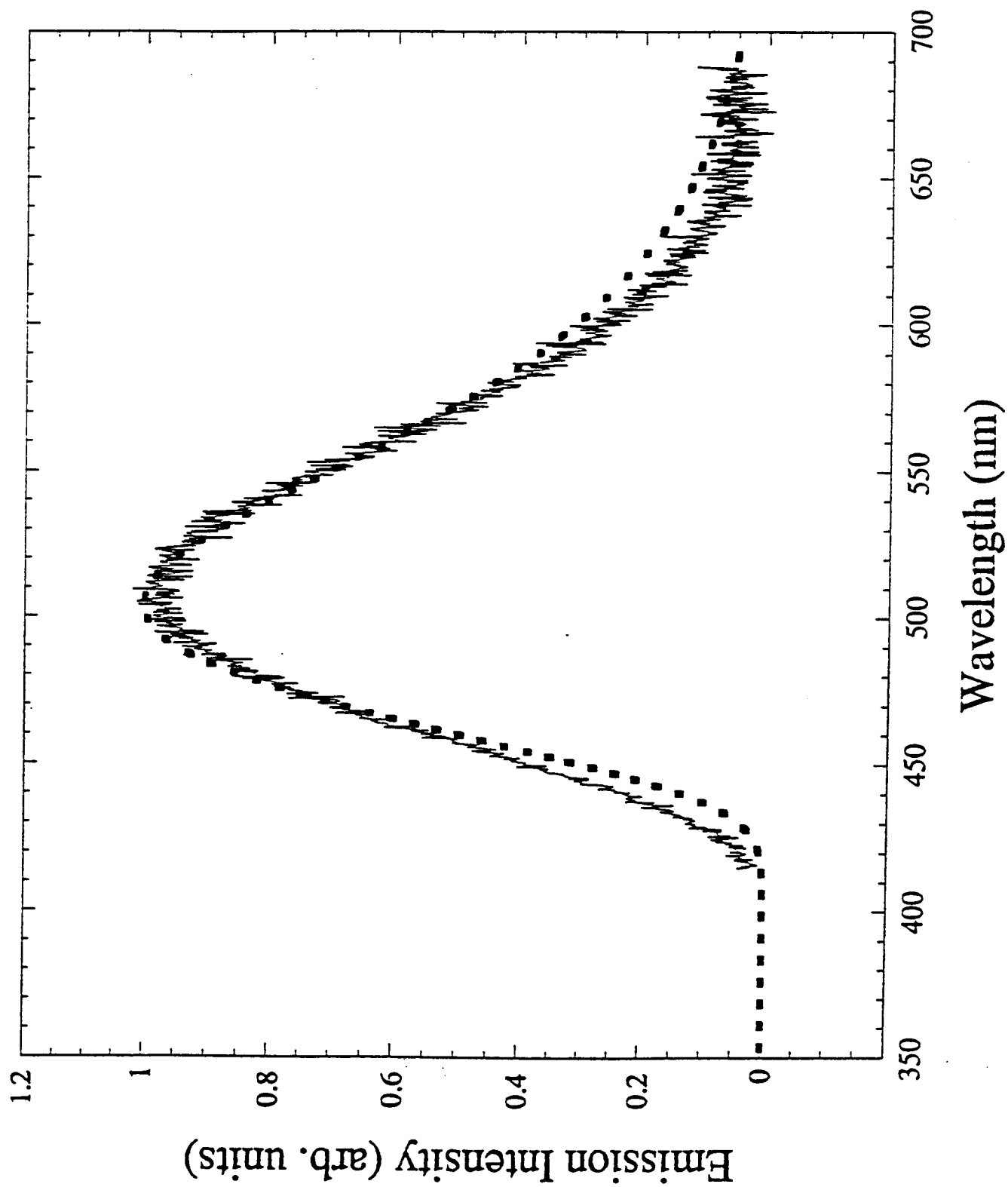
16. Dong, Y., unpublished results.

Figure Captions

1. Electronic absorption spectra for $Cd_4(SC_6H_5)_{10}^{4-}$ (·········) and $Cd_4(S-NB)_{10}^{4-}$ (- - - - - - -) in methanol as solvent.

2. Electronic Stark effect spectrum of **1** at 77 K.

3. Instrument and background corrected experimental (——) and calculated[14] (- - - - - -) emission spectra for **1** in methanol as solvent.
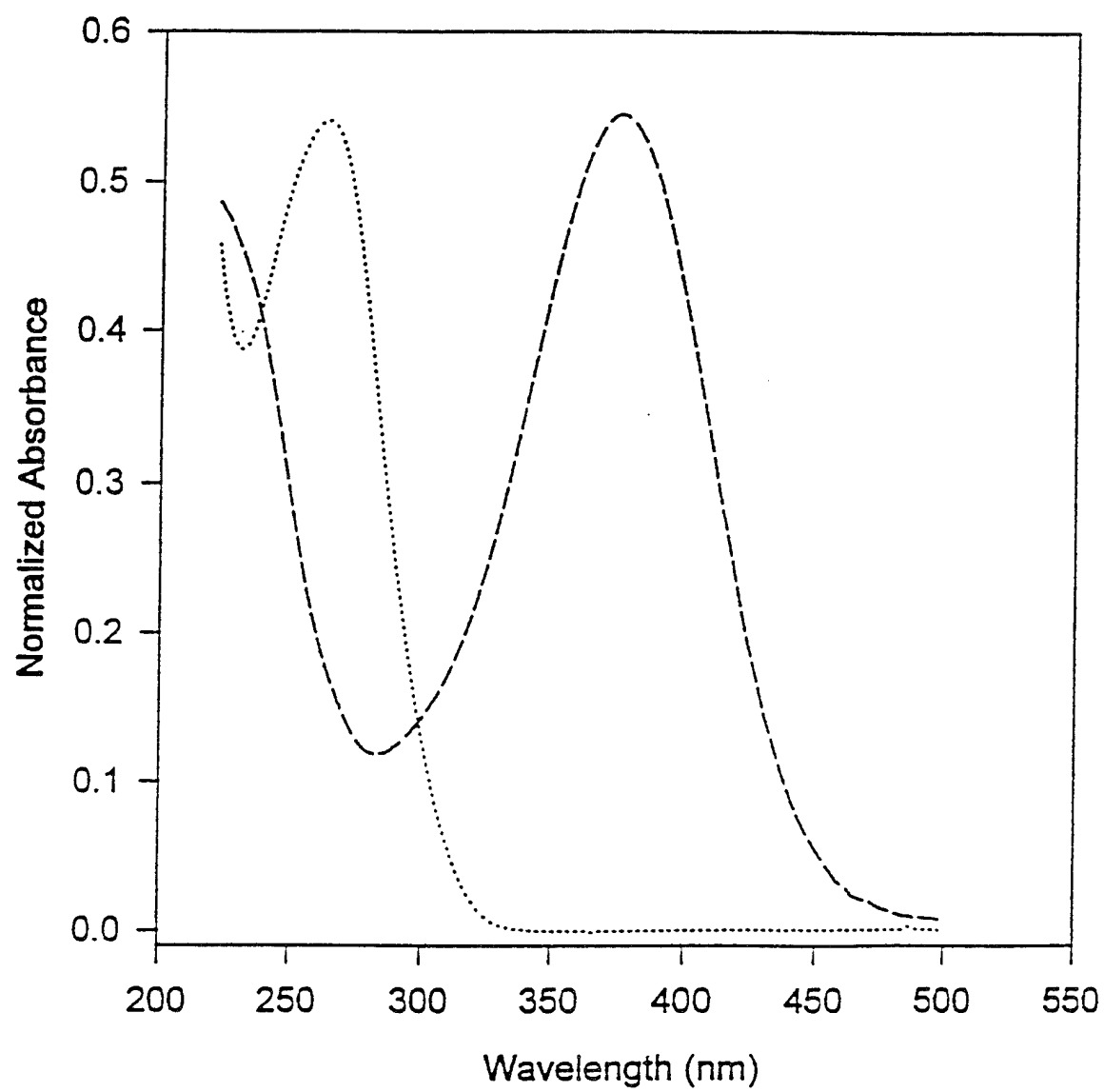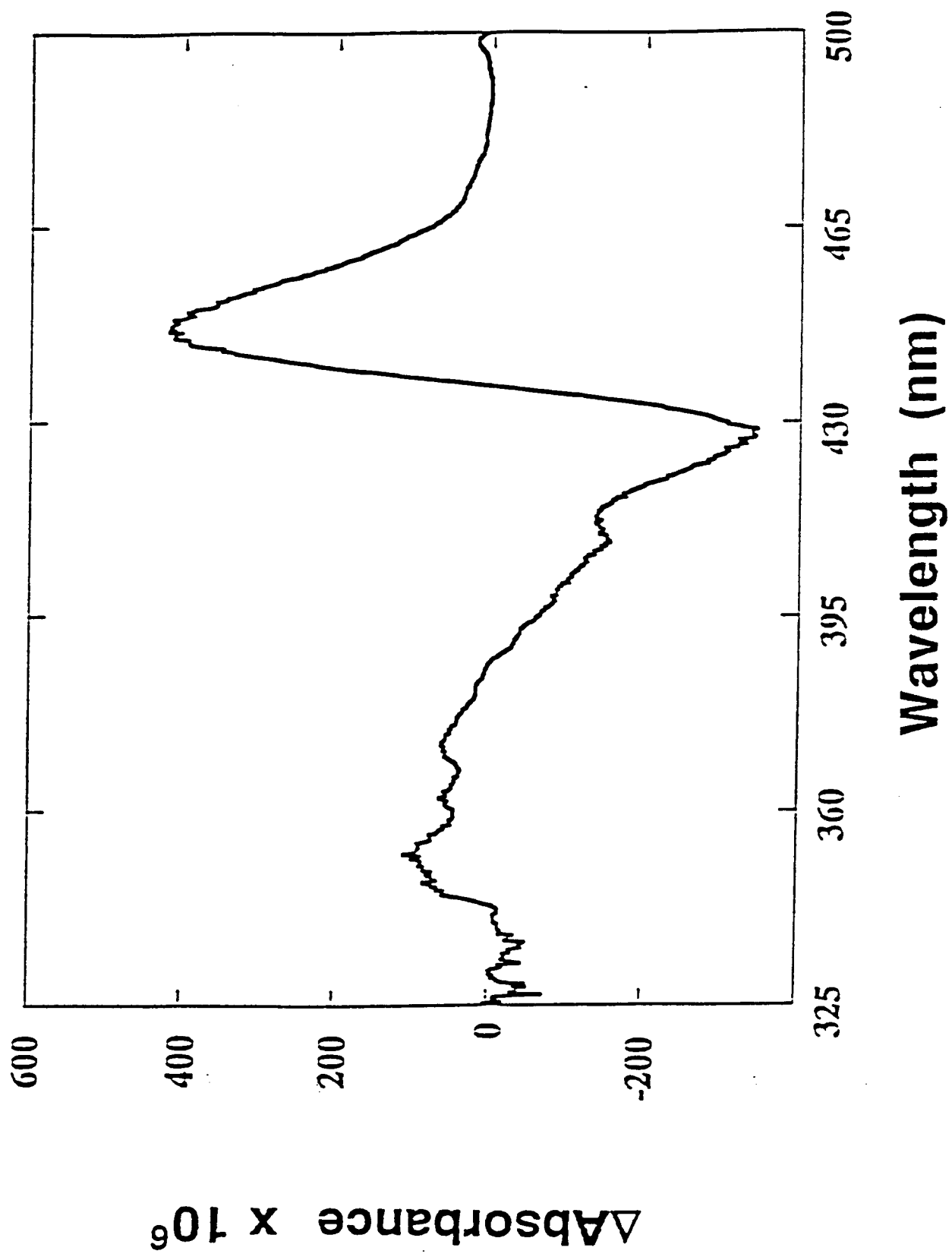
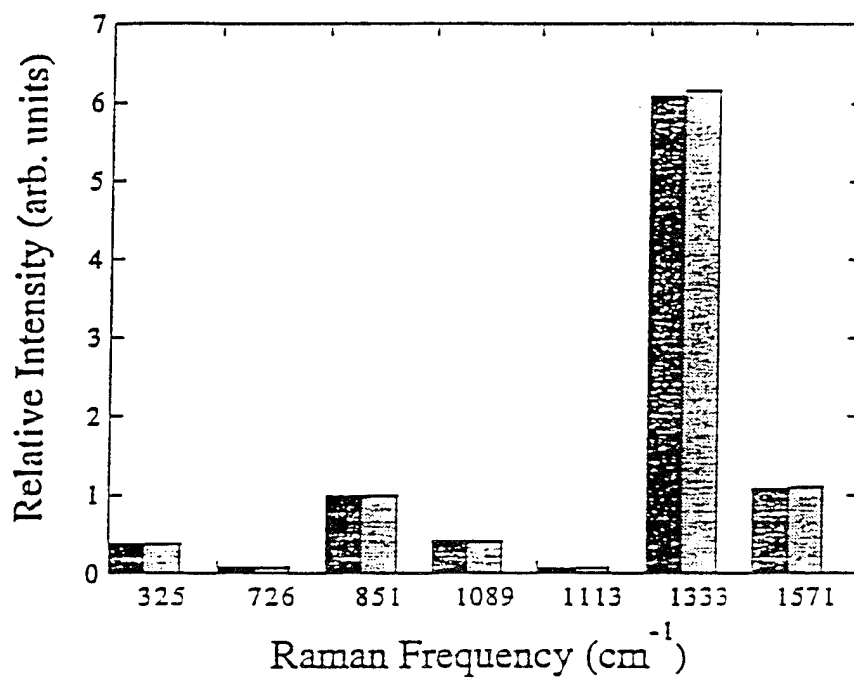Wavelength (nm)

ΔAbsorbance x 10^6

Figure S-1. Instrument-response-corrected Raman scattering intensities (shaded bars) and calculated Raman scattering intensities (solid bars) for 1 based on 351 nm excitation.

Table I.   Preliminary Structural and Franck-Condon Charge Transfer Data for

$Cd_4(S\text{-}NB)_{10}{}^{2-}$

Raman shift, cm^{-1}	Relative scatering intensity	$|\Delta|$	χ'_{vib}[a]	Preliminary assignment[b,c]
325	0.38	1.9	590 cm^{-1}	$\nu_{Cd\text{-}S}$
726	0.08	0.4	50	?
851	1.00	1.1	500	$\delta_{N\text{-}O}$ (symmetric deformation)
1089	~0.4[d]	0.5[d]	160[d]	$\nu_{C\text{-}S}$ coupled to ν_1: ⬡
1113	0.07	0.21	25	$\nu_{C\text{-}N}$
1333	6.2	1.6	1800	$\nu_{N\text{-}O}$
1571	1.10	0.57	250	ν_{8a}: ⬡
2177	0.91	--	--	combination band (851 + 1333)
2419	0.67	--	--	combination band (1089 + 1333)
2655	1.74	--	--	$2\nu_{N\text{-}O}$

a. Single mode contribution to χ_{vib}. b. Roth, P.G.; Venkatachalam, R.S.; Boerio, F.J.; *J. Chem. Phys.*, **1986**, *85*, 1150. c. Joo, T.H.; Kim, M.S.; Kim, X. *J. Raman Spec.* **1987**, *18*, 57. d. Interference from solvent scattering (CH_3OH) precludes exact determination of scattering intensity, normal coordinate displacement and reorganizational energy contribution.

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